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Preservation of Superhydrophobic and Superoleophobic Properties upon Wear Damage

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Supporting Information

ABSTRACT: Superhydrophobicity and self-cleaning require a combination of surface topography and low-energy surfaces, where mechanical damage of the topography or contamination with oils lead to loss of the nonwetting properties. We show that such vulnerability can be solved by superamphiphobic (i.e., both superhydrophobic and superoleophobic) surfactant-coated aerogel surfaces. Using silica aerogels as model materials, the self-similar network structure allows fresh re-entrant surface topographies even after removal of the uppermost layer upon mechanical abrasion, and superoleophobicity suppresses oil contamination. Given the recent progress toward mechanically strong aerogels, we foresee that the concept can open routes for robust self-cleaning coating technologies.

KEYWORDS: *oil-repellent, water-repellent, robustness, aerogel, topography*

The extreme water-repellency of biomimetic superhydrophobic surfaces, as inspired by Lotus plant leaves and butterfly wings, is appealing not only because of its scientific background but also for wide range of technological applications including self-cleaning, anti-icing, and microfluidics.[1−8] Such wetting properties arise from the interplay of surface topographical patterns and low-energy surface coatings, manifesting as high water contact angles and low sliding angles. Even if having attractive nonwetting properties, their practical use in real-life conditions is severely limited by durability issues.[9] For example, mechanical abrasion causes damage to the topographical patterns. As the patterns are essential to support the trapped air layer of the Cassie nonwetting state, the damage therefore can lead to undesired pinning of water droplets. The droplet pinning is also promoted upon damage of the hydrophobic surface layers, taken the underlying topographies often consist of less hydrophobic materials. In addition, superhydrophobic surfaces are typically easily wetted by oily liquids, leading to organic contamination and loss of water repellency. Therefore, identification of concepts for surfaces with long-lasting oil-repellent superhydrophobic properties would allow great benefits for future technologies.

Different strategies have been recently proposed to improve wetting robustness of superhydrophobic surfaces. In addition to repelling water, superoleophobic surfaces repel oily liquids with low surface tensions and thus make the surface resistant against organic contamination;[10,11,13] however, the re-entrant surface curvature that enables superoleophobicity usually also makes such surfaces more fragile. Durability against abrasion has been previously improved using three different approaches. (1) The first approach comprises thin films that are mechanically sufficiently rigid to withstand abrasion under given circumstances. Examples include a superamphiphobic nanostructured silica film that resists sand abrasion,[12] a superhydrophobic fabric that resists abrasion by another soft fabric,[14] and ink repellent superoleophobic silicon pillar arrays for printing technologies.[25,26] (2) The second approach deals with self-healing of thin films, which has the capability to recover the surface properties by renewal of the damaged surfactant layer,[15−17] or by reorientation of dangling chains.[18] Usually only the chemical composition of the surface is modified through self-healing, i.e., not the topography, and may require minutes to hours to complete,[15−17] a vulnerable period during which the surface has low contact angle (CA) and oily contamination may take place. (3) The third approach deals with preservation of both the topography and low-energy surface, even when part of the surface layer is removed. The important advantage of the third approach over self-healing is that the surface remains nonwetting immediately after abrasion. Relevant examples showing the preservation of superhydrophobic properties upon abrasion include a spray-cast polymer−clay composite film[19] and a organosilica foam.[20] Importantly, the third approach has only been demonstrated for superhydrophobic surfaces, not for superoleophobic surfaces, which are more challenging to construct as they require in addition to a low surface energy and surface roughness also a multivalued topography (i.e., with re-entrant texture).

Our hypothesis was that (1) a topographical pattern can exist after damage due to re-entrant self-similar network structure remaining in the underlying layers even if the topmost layer is removed by abrasion, and (2) suppressed oil contamination requires also superoleophobicity, allowed by the combination of

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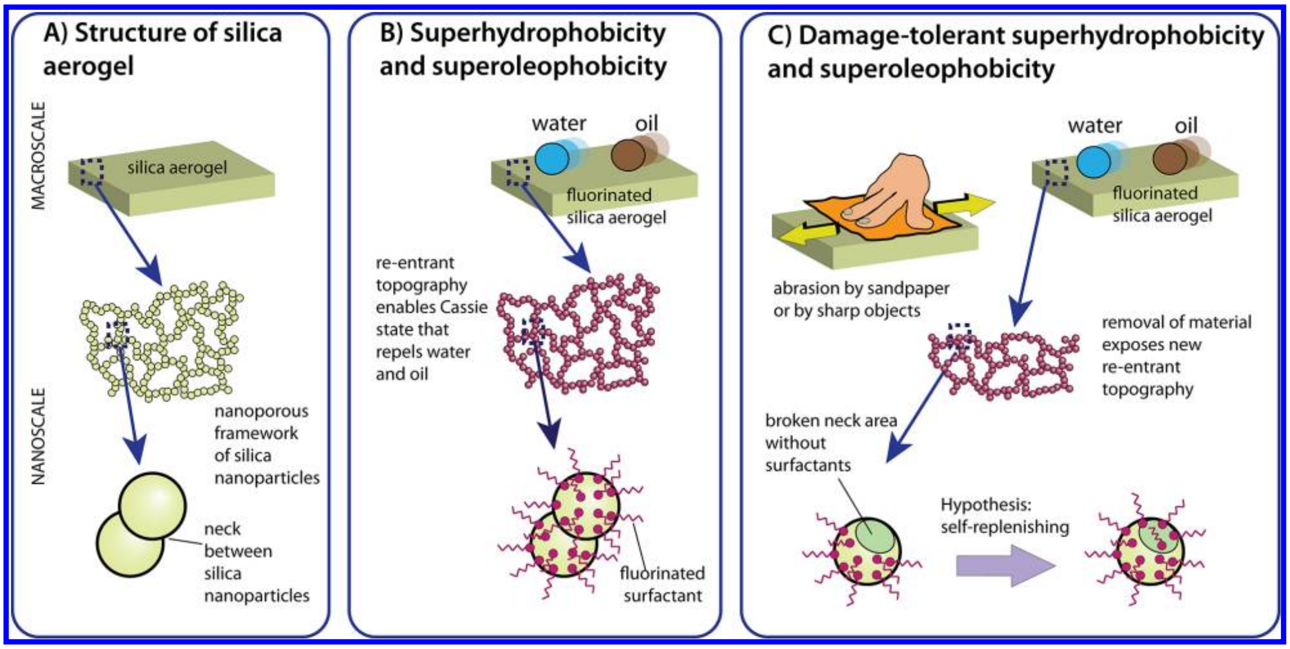

Figure 1. (A) Schematic representation of silica aerogel with its fractal-like bulk structure built from silica nanoparticles. (B) Silica aerogel has a re-entrant surface topography (i.e., overhangs) that renders it superhydrophobic and superoleophobic when modified with a fluorinated surfactant. (C) Mechanical abrasion by sandpaper or sharp objects leads to removal of part of the aerogel material and rupture of the necks that bond two nanoparticles together. Despite severe damage, the newly exposed aerogel surface still shows surface topography and superhydrophobic and superoleophobic properties with low contact angle hysteresis and low sliding angles. At the broken neck area, silanols become exposed, though the preservation of nonwetting properties suggests that the broken neck area gets replenished with surfactant molecules.

re-entrant pattern and fluorosurfactant. Therefore, we present a new approach toward durable superamphiphobicity (i.e., superhydrophobicity and superoleophobicity), using fluorosurfactant-coated silica aerogels as a model material. The surfaces are made from a commercial silica aerogel that is modified by chemical vapor deposition (CVD) with fluorinated surfactant (tridecafluoro-1,1,2,2-tetrahydrooctyl) trichlorosilane (FTCS). Silica aerogel is known to form self-similar networks of spherical silica particles having size in the nanometer scale (Figure 1A).[21,22] Therefore, it is a feasible model material for wetting studies, even if it suffers from mechanical brittleness. In this work we show that such an aerogel, when properly chemically modified, has superamphiphobic properties and we further show these nonwetting properties are retained and surprisingly even improved upon abrasion with sandpaper or sharp objects (Figure 1).

The contact angle (CA) hysteresis, defined as the difference between the advancing CA and receding CA, is an important parameter to characterize superhydrophobic and superoleophobic surfaces. A droplet on surfaces with low CA hysteresis rolls off with very low friction. In many cases, damage or contamination does not have much effect on the advancing CA, but it can decrease significantly the receding CA. Therefore, the CA hysteresis usually increases, leading to higher adhesion between surface and liquid, i.e., droplet pinning is promoted.

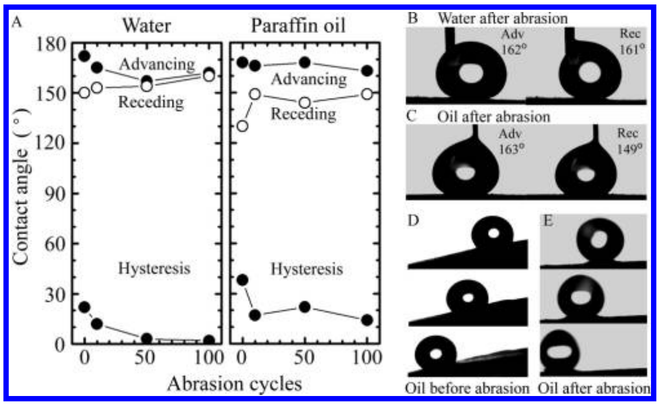

Figure 2. Wetting properties of the fluorosurfactant-coated silica aerogel surface before and after abrasion with sandpaper. (A) Contact angle data vs. abrasion cycles. (B) Advancing and receding CA for water after 100 cycles of abrasion. (C) Advancing and receding CA for paraffin oil after 100 cycles of abrasion. (D) Sliding angle of 10° demonstrated for paraffin oil before abrasion (frame intervals of 0.1 s). (E) Sliding angle of 2° demonstrated for paraffin oil after 100 cycles of abrasion (frame intervals of 0.12 s).

In this work, a silica aerogel was abraded by sandpaper, removing 660 μm of material after 100 abrasion cycles. Advancing and receding CAs are shown in Figure 2A as a function of abrasion cycles for water and paraffin oil. Advancing and receding CAs for water are 172 and 150° before abrasion, respectively, corresponding to CA hysteresis of 22°. For paraffin oil, the initial advancing and receding CAs are 168 and 130°, indicating a larger CA hysteresis. Even though the CA hysteresis is large, plastrons were observed when the modified silica aerogel was immersed in water or oil (see Figure S1 in the Supporting Information). Curiously, upon applying abrasion, the advancing and receding CAs started to approach each other; in other words the CA hysteresis decreases (Figure 2A). For water, the CA hysteresis becomes eventually as small as 1° upon 100 abrasion cycles (Figure 2B) and for oil it reaches 14° (Figure 2C). The low CA hysteresis upon abrasion manifests also in reduced sliding angles. Figure 2D shows that a 5 μL paraffin oil droplet slides off easily at a small tilt angle of 10° before the abrasion. Moreover, after the 100 cycles of abrasion, the tilt angle becomes drastically reduced to 2° (Figure 2E). This indicates that upon abrasion the surface has become highly repellent to oils and also water. A video of water and oil droplets rolling off the surface after abrasion by sandpaper and after scratching by a sharp object is available in the Supporting Information.

In contrast to most superhydrophobic and superoleophobic surfaces, the liquid repellency in this work exhibits high tolerance against mechanical damage, i.e., damage does not deteriorate the wetting properties. We suggest that this is caused by the nanoporous self-similar aerogel framework structure that essentially preserves the multivalued topography even upon abrasion, and in addition by deposition of surfactant in the interior of the aerogel. SEM micrographs before abrasion show that the aerogel surface contains micrometer scale roughness features that have an additional nanoscale roughness from the silica nanoparticles (Figure 3A, B). After abrasion with sandpaper (Figure 3C, D), the surface is smoother at the micrometer scale, though nanoscale roughness features similar as in the original aerogel surface are found (Figure 3B). When the surface is scratched with a sharp object such as a knife, severe abrasion is observed at macroscale, though also in this case nanoscale roughness features (Figure 3E, F) are similar as in the original aerogel surface (Figure 3B). It demonstrates that the silica aerogel has a nanoscale topography that is tolerant to damage, as a fresh surface with nanoscale topography gets spontaneously exposed upon mechanical damage.

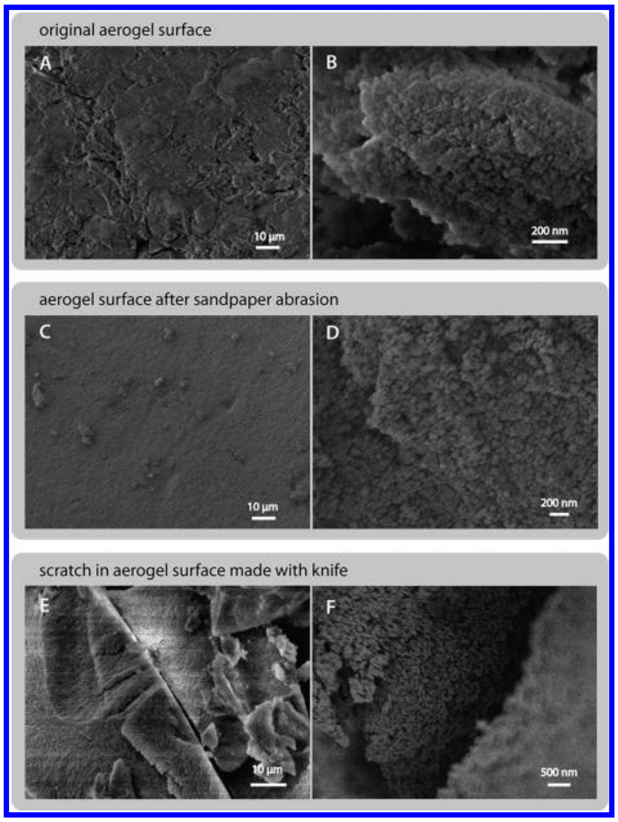

Figure 3. SEM micrographs of fluorinated silica aerogel (A, B) before abrasion, (C, D) after abrasion with sandpaper (100 cycles), and (E, F) after scratching with a knife. Images B, D, and F show that after mechanical damage the exposed aerogel surface has a similar nanoscale topography as before abrasion. This is due to the bulk structure of the silica aerogel, consisting of a nanoporous framework of silica nanoparticles.

In addition, the deposition of fluorinated trichlorosilane surfactant in the interior of the aerogel ensures the low surface energy and the preservation of nonwetting when the top layers are removed. According to X-ray photoelectron spectroscopy, the samples before abrasion and after 10, 50, and 100 cycles of abrasion have very similar chemical composition and show a fluorine content of approximately 42 at %. Though it is remarkable that upon damage the newly created surface at the broken necks does not contribute to increase of the contact angle hysteresis (Figure 2), as would be caused by increased surface energy of uncoated silica. We expect that upon abrasion the thin necks between two silica nanospheres break, being weak links (see Figure 1C), and the bare silica surface at the site of the broken neck becomes exposed locally. Based on the preservation of the low contact angle hysteresis, we hypothesize that the exposed silica surface gets replenished by fluorosurfactant. Possible sources for replenishing may originate from partially defective monolayers where the silane does not react with the underlying substrate,[23] or from excess of the surfactant remaining inside the pores. As the broken surface area is relatively small, only a low number of fluorosurfactant molecules are sufficient to replenish the exposed areas, thereby providing healing of the coating. The increase in receding contact angle upon abrasion may be caused by the removal of defects on the aerogel surface.

We finally point out that in this study, the silica aerogels have been used only as a model material to demonstrate the concept of preservation of superhydrophobic and superoleophobic properties upon wear damage. Future work could be devoted to enhancing the mechanical properties of superamphiphobic aerogels while maintaining a framework structure with re-entrant topography, for example, using mechanically strong and tough aerogels combining silica with polymers,[24] or using aerogels reinforced using carbon fibers, nanotubes, clay, or graphene.

In summary, superhydrophobic and superoleophobic surfaces have been obtained from surfactant-modified silica aerogels with low sliding angle for water and paraffin oil. We propose superhydrophobic and superoleophobic bulk materials with re-entrant features in nanoscale as a new concept in designing damage-tolerant superhydrophobicity and superoleophobicity. In contrast to most superoleophobic surfaces that have poor durability of their liquid repellency after damage by mechanical abrasion, the presented superoleophobic surfaces still have high liquid repellency with low CA hysteresis and sliding angle for both water and paraffin oil.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Video S1 demonstrates superhydrophobic and superoleophobic nonwetting properties upon sand paper abrasion and scratching with metal tweezers. Experimental methods. Photographs of plastron on aerogel surface immersed under water and oil and SEM image of the original aerogel surface. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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